

### ABSTRACT OF THE DISCLOSURE

A polymerization process comprising initiating a first polymerization of monomers using an initiator functionalized with an ATRP initiating site, wherein the first polymerization is selected from the group of cationic polymerization, anionic polymerization, conventional free radical polymerization, metathesis, ring opening polymerization, cationic ring opening polymerization, and coordination polymerization to form a macroinitiator comprising an ATRP initiating site and further initiating an ATRP polymerization of radically polymerizable monomers using the macroinitiator comprising an ATRP initiating site. Novel block copolymers may be formed by the disclosed method.